

## Luminescence studies during combustion synthesis of a long afterglow phosphor $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{Dy}^{3+}$

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The long glow persistent phosphor  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{Dy}^{3+}$  has been synthesized through combustion route.  $\text{SrAl}_4\text{O}_7$  and  $\text{SrAl}_2\text{O}_4$  are identified as the intermediate products formed at different temperatures during the synthesis of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{Dy}^{3+}$ . The photoluminescence and afterglow emission of the intermediate products have been systematically studied. The photoluminescence and afterglow emission profiles of the intermediate products varied with the temperature of synthesis. For a sample with similar aluminate phases (at a particular synthesis temperature) the  $\lambda_{\text{AGL}}$  and  $\lambda_{\text{PL}}$  are different. However, for  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{Dy}^{3+}$  annealed at 1200-1300°C, the AGL and PL emissions are similar.

Europium activated strontium aluminates are well-known long afterglow phosphors. Strontium aluminate phosphors like  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ ,  $\text{SrAl}_4\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ ,  $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}^{2+}, \text{Dy}^{3+}$  and  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{Dy}^{3+}$  are of special interest for their efficient emission in the visible region<sup>1</sup>. Moreover, these phosphors do not involve any radioactive isotope for continuous excitation. The utility of such phosphors depends on their luminescence performance which depends significantly on the powder characteristics. Therefore, different processes of phosphor synthesis are currently an active area of research. Usually, aluminates are prepared by solid-state reaction route or wet chemical routes like combustion synthesis. During preparation of such phosphors many intermediate aluminates are known to be formed. In this study,  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{Dy}^{3+}$  have been synthesized through combustion route. Luminescence properties of these intermediate compounds were investigated. The photoluminescence (PL) and afterglow luminescence (AGL) of these intermediate compounds have also been studied. An attempt has been made to correlate the observed luminescence with these intermediate compounds formed at different temperatures of synthesis.

### Experimental Procedure

Stoichiometric amount of  $\text{SrNO}_3$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , and  $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  were taken to prepare the polycrystalline  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{Dy}^{3+}$ . All

the reactants were of analytical grade. About 2 mol % of boric acid was added as flux. The ratio of  $\text{Eu}^{3+}$  to  $\text{Dy}^{3+}$  was maintained at 1:2 mol% in all samples. Stoichiometric ratio of urea was taken as a fuel. All the reactants were dissolved in distilled water and heated in hot plate at 80°C until the gel formation. Subsequently, the gel was placed inside the muffle furnace which was preheated at  $600 \pm 10^\circ\text{C}$ . The sample was self-ignited and a white fluffy material was produced. The precursor so obtained was given heat treatment at 700°C, 800°C, 900°C, 1000°C, 1100°C, 1200°C and 1300°C under reduced atmosphere (2%  $\text{H}_2$ ) for 5 h.

The phase identification of synthesized powder samples was carried out by using a Siemens D-500 XRD spectrometer ( $\text{Cu K}\alpha: 1.541\text{\AA}$ ). The photoluminescence emission and excitation measurements were carried out with a Jyobin Yvon Spectrofluorimeter Fluorolog-3 equipped with 450 W Xenon lamp as excitation source. The excitation and emission monochromators were set at 1 nm band width. For recording afterglow emission the sample was irradiated with a 4 W UV lamp (356 nm) for 5 min and then the sample was placed inside the spectrofluorimeter. The AGL was recorded with emission monochromator set at 1 nm band width and the excitation lamp was switched off. Thermo stimulated luminescence measurements were carried out using TLD-Reader (Nucleonix, India) in the temperature range of 40-410°C under linear heating rate of 10°C/s. Samples were irradiated using a 4 W UV lamp (365 nm) for 5 min prior to afterglow and

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thermoluminescence measurements. All the samples were stored for 24 h in dark prior to irradiation and luminescence measurements to avoid interference from room light. The delay time between UV irradiation and afterglow measurement was 30 s for all samples.

### Results and Discussion

Figure 1 shows the XRD spectra of the samples annealed at different temperatures. The XRD was recorded at different stages of annealing, to monitor the formation process of Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>. At 700°C, the sample was highly amorphous. Upon further calcination at 800°C, the SrAl<sub>4</sub>O<sub>7</sub> and SrAl<sub>2</sub>O<sub>4</sub> signatures were developed. Further rise in temperature to 900°C made SrAl<sub>2</sub>O<sub>4</sub> as the prominent phase. However at 1000°C, the SrAl<sub>4</sub>O<sub>7</sub> phase became prominent instead of SrAl<sub>2</sub>O<sub>4</sub>. Beyond this temperature, formation of Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub> started as seen here in the temperature range of 1100-1300 °C. The SrAl<sub>4</sub>O<sub>7</sub> phase was not perceptible at 1100°C. However, weak signals for SrAl<sub>2</sub>O<sub>4</sub> continued to be present at this temperature. As the temperature is further raised the Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub> signals gained intensity and also the crystallinity of the phase improved. For the samples fired at 1200°C and 1300°C no trace of SrAl<sub>4</sub>O<sub>7</sub> was detected because at this temperature SrAl<sub>4</sub>O<sub>7</sub> is not stable and it reacts with SrAl<sub>2</sub>O<sub>4</sub> to yield pure Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub><sup>2</sup>.

Figure 2 shows the emission spectra of samples heated at different temperatures. Photoluminescence could not be detected from samples heated at 700-800°C. The sample at 900°C exhibited emission at 515 nm as shown in Fig. 2a. SrAl<sub>2</sub>O<sub>4</sub> is known to emit<sup>2</sup> around 515 nm. The phase observed at 900°C had major content of SrAl<sub>2</sub>O<sub>4</sub> as discussed above. Therefore, the 515 nm emission observed at 900°C can be attributed to SrAl<sub>2</sub>O<sub>4</sub>. Figure 2b shows that increasing

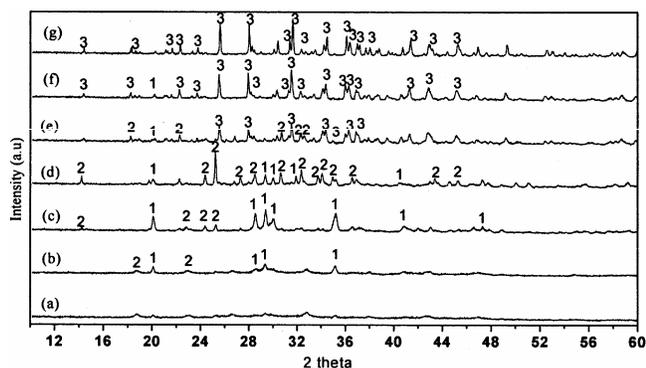


Fig. 1—XRD pattern of strontium aluminate synthesized through combustion route and annealed at different temperature (a)700°C, (b)800°C, (c) 900°C, (d) 1000°C, (e) 1100°C, (f) 1200°C and (g) 1300°C (1-SrAl<sub>2</sub>O<sub>4</sub>, 2- SrAl<sub>4</sub>O<sub>7</sub>, 3- Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>)

the temperature to 1000°C, the sample exhibited emission at 466 nm. The predominant phase formed at this temperature was SrAl<sub>4</sub>O<sub>7</sub> as the XRD pattern has shown minimal presence of other phases (Fig. 1). Hence, we have ascribed the observed emission<sup>3</sup> at 466 nm to SrAl<sub>4</sub>O<sub>7</sub>:Eu<sup>2+</sup>. As mentioned earlier, at 1100°C Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub> has become the major phase and the emission observed for this sample was around 482 nm (Fig. 3c). The shift from 466 nm (seen at 1000°C) to 482 nm could be the result of the convolution of emission from Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>:Eu<sup>2+</sup> and SrAl<sub>4</sub>O<sub>7</sub>:Eu<sup>2+</sup>. Subsequently at

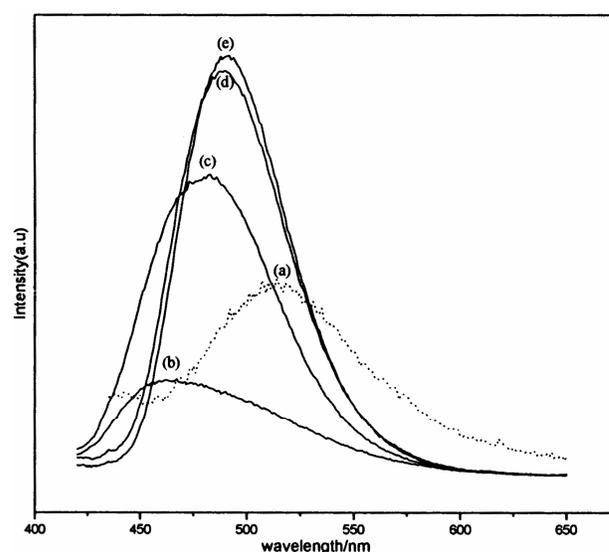


Fig. 2—PL emission spectra ( $\lambda_{\text{exc}}=396$  nm) of strontium aluminate synthesized through combustion route and annealed at different temperature (a) 900°C, (b) 1000°C, (c) 1100°C, (d) 1200°C and (e) 1300°C

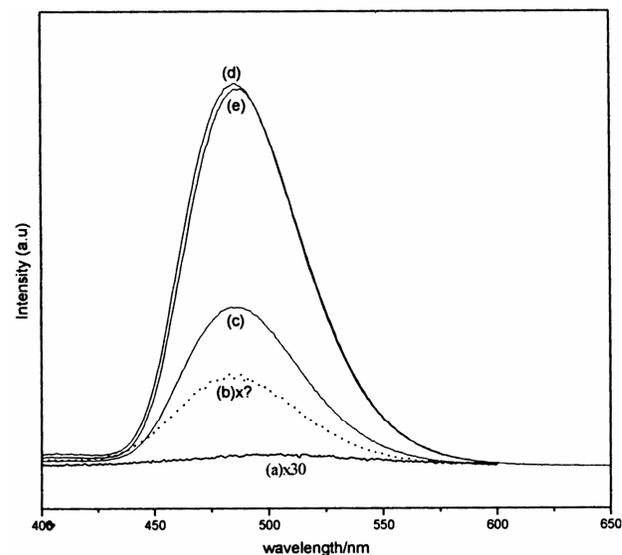


Fig. 3—Afterglow emission of samples fired at 900°C, (b) 1000°C, (c) 1100°C, (d) 1200°C and (e) 1300°C

1200°C only  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$  was present. Therefore, the emission at this temperature was seen around 490 nm.  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$  is known to emit<sup>4</sup> around 490 nm. The marginally increased 490 nm luminescence at 1300°C was due to the better crystallinity of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ .

#### Afterglow emission

Afterglow spectra of combustion-synthesized samples prepared at different temperatures are shown in Fig. 3. Unlike in case of samples prepared through solid state route, the samples here annealed at 700-800°C did not show any perceptible AGL or PL. Sample fired at 900°C exhibited very weak afterglow emission at 510 nm with negligible persistence time. XRD indicated formation of  $\text{SrAl}_2\text{O}_4$  along with signature of  $\text{SrAl}_4\text{O}_7$ . At this temperature earlier PL was also observed around 515 nm which is in agreement with the AGL observation<sup>5</sup>.

The phosphor obtained at 1000°C exhibited AGL at 485 nm contrary to the PL observed at 466 nm. According to the XRD profiles, at this temperature  $\text{SrAl}_2\text{O}_4$  and  $\text{SrAl}_4\text{O}_7$  existed with later being the dominant one. Probably  $\text{SrAl}_2\text{O}_4$  had more number of necessary defects contributing to the AGL than in the major compound  $\text{SrAl}_4\text{O}_7$ . EDS (energy dispersive spectrum) studies indicated that dysprosium was not distributed uniformly between both the phases. It is known that presence of dysprosium helps in increasing the trap density. Therefore, the phase with minimum dysprosium is expected to have low trap density. This may be the reason for seeing the shift in the AGL emission towards green region. At 1200-1300°C the  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  was the only compound present and the AGL and PL were expectedly observed at 490 nm.

Chen *et al.*<sup>6</sup> in their study of host compositions on the afterglow have also observed AGL at different wavelengths. However in their study, they have recorded only the AGL from the samples containing multiple aluminates. The Al/Sr ratio had an effect on

the  $\lambda_{\text{AGL}}$  but there was no systematic trend between the observed  $\lambda_{\text{AGL}}$  and the Al/Sr ratio. They have attributed the variation in the  $\lambda_{\text{AGL}}$  to the variation of  $\text{Eu}^{2+}$  coordination environment and the difference in the strength of crystal field for  $\text{Eu}^{2+}$  in the strontium aluminates. It is assumed that in the afterglow materials both the PL and AGL emissions are from the same centre. Therefore, any change in the crystal field strength or coordination environment of  $\text{Eu}^{2+}$  should have resulted in emission at the same wavelength in both the PL and AGL. In our study we have observed that for the same sample, the  $\lambda_{\text{AGL}}$  and  $\lambda_{\text{PL}}$  were different as discussed earlier. The trap dynamics in case of persistent luminescence is very complex and probably a minor change in the host composition reflects considerably in the luminescence characteristics.

#### Conclusions

The long glow persistent phosphor  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$  was successfully synthesized through combustion synthesis. The intermediate products formed at different temperatures were identified as  $\text{SrAl}_4\text{O}_7$  and  $\text{SrAl}_2\text{O}_4$  and their photoluminescence and afterglow emission were systematically studied. The variation in  $\lambda_{\text{PL}}$  was due to the presence of different phases to different extent. For samples with similar aluminate phases the  $\lambda_{\text{AGL}}$  and  $\lambda_{\text{PL}}$  were observed to be different. However for  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$  prepared at 1200-1300°C the AGL and PL emissions were similar.

#### References

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